

EXHIBIT A

The logo for 'científica' features the word in a bold, lowercase, sans-serif font. A small, stylized graphic element, resembling a pen nib or a sharp point, is positioned above the letter 'i'.

Nanocrystalline Materials

Technology White Papers
nr. 4

A large, dark, grainy image occupies the lower two-thirds of the cover. It appears to be a microscopic view of a material surface, showing numerous bright, irregularly shaped spots and clusters against a dark background, likely representing nanocrystalline structures.

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NANOCRYSTALLINE MATERIALS

Technology White Papers nr. 4

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Origin of content

The free reports in this series are extracted from the technology reports that make up the Nanotechnology Opportunity Report collection and are designed to offer an introduction to the variety of technologies that fall under the nanotechnology umbrella. The full reports also include 'opportunities' sections, covering the various applications of the technology and their effects on markets, and a list describing the companies involved in the technology.

Introduction

This report covers bulk nanocrystalline materials and coatings. Metals and ceramics (these being metal oxides in the context of this report), both bulk and in coatings, make up most of the content of the report. Both these materials are generally made up of crystals the size of which are measured in micrometers. Reducing the size of the crystals can have quite dramatic effects on the properties of the bulk material, particularly increasing strength.

The creation of nanocrystalline materials is in its infancy. A few companies are starting to commercialize products and significant growth can be expected, penetrating the huge markets for structural materials and coatings. The new products will not be without competition from other materials, especially nanocomposites, but there are markets where these new materials will be the favored choice in the future.

Nanocrystalline materials

Nanostructure and properties

Bulk metals and ceramics and coatings

Metals and ceramics are generally polycrystalline, meaning that they consist of many randomly oriented crystalline regions, or grains. Reducing the size of the grains (also referred to as crystals or domains) in existing materials can have a big impact on bulk material properties. As the grain size in a metal, for example, moves into the nanoscale, an increasing proportion of the atoms in the solid are found on grain boundaries, where they behave differently from those not on boundaries. Their behavior starts to dominate the behavior of the material (at roughly 5 nm, 50% of the volume will be grain boundaries).

Note that a nanocrystalline material need not just be a bulk solid or surface but can be a powder, or nanopowder, thus there is overlap of the use of the terms nanocrystal and nanoparticle for some materials. In general, though, the important properties of nanocrystalline nanoparticles stem from their nanoparticulate nature and will not be considered here (this applies, for example, to nanocrystalline semiconductor quantum dots, where size is the critical property). This report will focus largely on bulk nanocrystalline materials. Nanopowders can, however, be the source material for making nanocrystalline solids and coatings.

It is often stated that as grain sizes move into the nanoscale, metals get stronger and harder (and more brittle) while ceramics become more ductile (malleable). This is an approximation, though, and in fact the reality is more complex and dependent on what part of the nanoscale the grain sizes are in. The approximation stated works, for example, in metals with grain sizes down to about 10 nm, below which a decrease in hardness and strength is seen. In ductile nanocrystalline ceramics, grain sizes are often below this size. The traditional theory behind the change in hardness with grain size is the Hall-Petch relation, which states that hardness increase is inversely proportional to the square root of the grain size (the basis of the effect, put simply, is the limiting of the spread of dislocations, or breaks in the crystal structure, by an increasing number of grain boundaries). This makes for dramatic increases in hardness when going from normal grain sizes to around 10-20 nm.

(Note that grain size is not the only way in which the spread of dislocations can be controlled—creating layered materials can achieve the same effect.)

Other properties of nanocrystalline metals, apart from increased strength and hardness, include higher electrical resistance, increased specific heat capacity, improved thermal expansion properties, lower thermal conductivity and improved magnetic properties.

In ceramics, the increase in ductility when they become nanocrystalline is accompanied by improved toughness (the ability to withstand an impact or applied strain), or reduced brittleness, and improved ability to bond to a metal component. The toughness leads to increased wear resistance (2-4 times that of a traditional ceramic coating) but, somewhat counter-intuitively, grinding and polishing, which is often performed after laying down a ceramic coating, is actually easier with nanocrystalline ceramics.

Increased ductility is especially valuable in ceramics, where brittleness is often a major problem, and superplasticity has been observed in both nanocrystalline metals and ceramics at around 200°C, making for easier forming of materials. The most important impact of increased ductility in ceramics is on ceramic coatings for machinery that resist wear and corrosion. These materials generally fail not because of wear but because of insufficient toughness.

Research into new nanocrystalline ceramic coatings holds promise, with materials such as tungsten-carbide cobalt, chrome oxide and yttria stabilized zirconia being investigated.

The ductility of nanocrystalline ceramics also creates the possibility of drawing them into wires, offering applications based on the superconducting properties of some ceramics.

In metals it is the improved strength that is most sought after, and the increased stiffness can actually be a problem, since ductility is useful not just in manufacturing but also in terms of behavior on impact, an important consideration in cars, for example.

To give an idea of the changes that can be achieved in metals, Rensselaer Polytechnic researchers measured the strength of nanocrystalline copper and found it to be 5 times harder than conventional copper. In fact today's strongest steels have about 10% of the theoretically possible maximum strength.

Loss of ductility in nanocrystalline metals can actually be avoided. This can be achieved by creating a mixture of nanoscale and microscale grain structures. Late in 2002, researchers at Johns Hopkins University managed to create copper that was 75% nanocrystalline with 25% of microcrystalline grains dispersed in the material. It proved to be 5-6 times the strength of normal copper but without any loss in ductility. A ceramic structure with microscale grains embedded in a predominantly nanocrystalline matrix has also been found, by the US's Office of Naval research, to produce the best properties for their aluminum and titanium oxide ceramic coatings.

Note that there are competing approaches to making stronger steels while retaining ductility. Traditional steel has carbon particle inclusions; in 2001, a group at NKK in Japan demonstrated a way of including nanoparticles in the rolling process for steel to make these inclusions smaller, resulting in a new steel that is significantly stronger than existing varieties but with the formability required for uses in creating car engine parts or body components. Toyota, which was involved in the project, is already using the new steel.

Alternatively, crystalline structure can be avoided altogether, by creating amorphous metals, in which there is no particular pattern in the atomic order (glass is a classic example of an amorphous material). In 2001, the US Department of Energy's Idaho National Engineering and Environmental Laboratory developed a spray-on super-hard (and corrosion-resistant) steel amorphous coating that proved remarkably resilient, approaching the best tungsten-carbide coatings in hardness (the application of heat can convert this amorphous coating into a nanocrystalline form), with both strength and hardness reaching 45% of the theoretical maximum. While only coatings have been achieved so far, the hope is to be able to build thick industrial steel sheets out of this material.

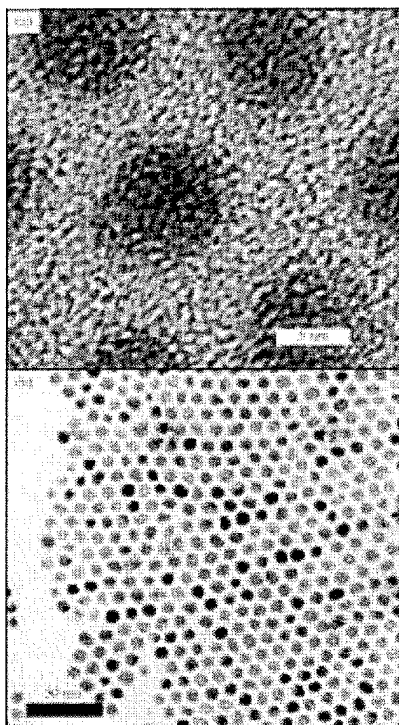
Chemical reactions and catalysis

Increased reactivity is also seen in bulk nanocrystalline materials because of increased surface area. This can be useful with respect to direct chemical reactions or in terms of catalytic activity. An example is the lithium tin nanocrystalline alloy made at Brookhaven National Labs early in 2002, in which the 20-30 nm grain size gave improved reactivity, and potentially a more powerful battery. Also, back in 1999, researchers at MIT started creating nanocrystalline high temperature catalysts (used, for example, in the catalytic combustion of natural gas—an area of great interest at the moment) that could be created at lower temperatures than were normally required but would still withstand the high operational temperatures.

Nanostructured cerium ceramics have been shown to offer catalytic activation for sulfur dioxide reduction and carbon monoxide oxidation at significantly lower

temperatures than traditional versions of these catalysts, and they have also shown greater resistance to poisoning (the loss of catalytic reactivity caused by contaminants). Some materials only develop catalytic activity once they become nanostructured, an example being cadmium selenide, which is not normally photocatalytic but becomes so when nanocrystalline, and offers the ability to 'fix' (a term taken from photosynthesis) waste carbon dioxide.

Other nanocrystalline materials of note



TEM image of (hcp) Co nanocrystals (NCs). Colloidal synthetic methods allow Co NCs to be produced in several distinct crystal polymorphs with varying degrees of crystal perfection. Courtesy of IBM.

Nanocrystalline and nanoporous silicon showed promise in a few research results in 2001 because of their ability to emit light. Nanocrystalline silicon has properties, in addition to electroluminescence (of interest for semiconductor laser applications), such as photoluminescence, thermally-induced acoustic emission, and refractive index changes that can be controlled. The attraction here is the compatibility with silicon-based electronics. Not much research of note has been seen in this area in 2002, however.

Towards the end of 2002, though, nanocrystalline nanoporous silicon was shown to have a property applicable to a very large and dynamic market, that of flat panel displays. Researchers at Tokyo University created nanocrystalline silicon film with a pore structure that varied with depth and in which the electrons could be accelerated to the surface, creating what the researchers called a 'vacuum-less cathode-ray tube'.

Nanocrystalline diamond is another interesting material. Argonne National Laboratory created a film of diamonds that are only 3-5 nm across (each containing around 1000 atoms) by using buckyballs (molecular cages of 60 carbon atoms) as a feedstock. The tiny size changed the electrical properties of the diamond film, when compared with normal diamond films, because of electron

transport at grain boundaries (aided by nitrogen), meaning that the diamond can be made to behave as a semiconductor (researchers at CSEM in Switzerland have achieved similar results). The advantage of diamond over silicon is its ability to tolerate extreme environments. It also exhibits much less friction than silicon, and is much stronger, which may be useful in microelectromechanical systems.

The relationship between nanocrystals and magnetism holds the possibility of making stronger permanent magnets. Grain size is already a factor in magnetic materials that

is controlled to achieve desired properties, especially the smallest possible magnetic domains in recording media. Below a certain size a grain is liable to spontaneously switch its magnetic orientation (this relates to the superparamagnetic limit). The latest materials for recording media have elongated grains that allow the total volume of a grain to remain above the limit while presenting a smaller surface profile. Theoretical limits are being approached in this area but in permanent magnets there is still a lot of scope, with some suggesting that 4-5 times the strength of current permanent magnets could be achieved if the ideal grain structure could be attained.

Finally, it should not be forgotten that nature is a master of nanomaterials and nanocrystalline materials are no exception. Many groups are working on borrowing from nature to make nanostructured materials, either by emulating natural processes or by modifying biomaterials directly (for example, by taking the shells of tiny marine organisms, called diatoms, and chemically modifying them). However, natural materials like this are not generally nanocrystalline in the sense of having multiple nanoscale crystal domains, but tend to be instead a more globally structured crystalline form. An example of some work done in this area, which does indeed produce a nanocrystalline material as an approximation of the material that nature produces, is research done on hydroxyapatite by MIT.

Hydroxyapatite is the main mineral component of bone and synthetic versions tend not to be anywhere near as strong as natural ones. MIT's version was built by coalescing nanoscale particles into a solid that was much closer to the strength of bone than traditional synthetic versions.

Production techniques

Materials can be made nanocrystalline using quite a wide variety of techniques.

For coatings, new techniques, such as pulsed laser deposition or electrodeposition, or variants of chemical vapor deposition techniques, have been developed that can coat a surface with nanocrystalline metals, semiconductors and other materials.

Thermal spraying is an increasingly popular way of converting the new generation of nanopowders into nanocrystalline coatings—heat is used to partially melt the powders so that they fuse when they form the coating. Varying the amount of melting can lead to different structures. A variation of this technique, using a plasma (a hot, ionized gas) into which nanoparticle agglomerates are fed, is used to produce the ceramic coating used by the US Navy (previously mentioned) and other ceramic coatings. The nanostructure is created by retaining some of the original nanoparticle structures (thus only limited melting can be allowed), or by mixing nanoparticles with different melting temperatures, or by allowing the nanostructure to form in the applied coat through the combining of non-miscible materials. This approach was used to achieve the useful mixture of nanoscale and microscale grains.

Electrodeposition is an old coating process but has been successfully customized to produce coatings with grain sizes down to 5 nm. It is a commercially attractive

process because it can be carried out at room temperature and can be used for large-scale production.

To create bulk materials that are nanostructured in three dimensions, powder compaction, crystallization of initially amorphous material, and severe plastic deformation processing are the leading methods but approaches such as electrodeposition have also been used.

Powder compaction methods involve first producing nanoscale particles which are subsequently fused together using combinations of pressure and heat. Nanoparticles can be made to partially melt and fuse at temperatures below the normal melting point of a material. These methods have been limited by the challenge of controlling contamination or oxidation of the high surface area particles that are the raw material, and the resulting materials also tend to be porous, but the methods offer the advantage of being able to combine different particles to create nanocomposites.

Severe plastic deformation (SPD) processing techniques are applicable mainly to metals. These methods all take advantage of the ability of the crystals within metals to subdivide into domains as small as 20 nanometers when they are subjected to large shearing strains while under high pressure, though crystal sizes a little below 100 nm are more common. The strain can be applied in a number of ways, such as extrusion, bending or twisting, or rolling.

SPD approaches have the advantage over powder methods for bulk solids that they can create nanocrystalline materials with minimal porosity and contamination.

SPD is scalable and is thus being pursued for commercialization. However, there is an inevitable additional cost and sometimes the resulting material contains unwanted stresses.

The super-strong but ductile copper made at Johns Hopkins University used a variant of deformation processes. Rolling created the nanostructure and subsequent annealing (a process involving heating to below the melting temperature, usually used to relieve stresses) led to the formation of some micrometer-sized grains.

Purdue University researchers made a serendipitous discovery in mid 2002 that seems obvious in retrospect. Shavings from working metals are, of course, subjected to great stress. The Purdue researchers discovered that the materials are often nanocrystalline as a result, offering the possibility of making nanocrystalline bulk materials out of waste that would normally be melted down and recycled.

Crystallization of amorphous materials can produce the finest scale nanostructures, but is limited to materials that can be first put into an amorphous state. However, approaches such as sol gel allow the creation of a wide variety of materials with a very well-controlled nanostructure (if not necessarily nanocrystalline) and have been used to make ultra-non-stick ceramic coatings.

The lithium tin nanocrystalline alloy made at Brookhaven National Labs, which was used as a high-performance electrode, was created using a rather original technique, reacting lithium hydride with tin oxide, but with more of the former than was needed to react fully. This produced a lithium tin alloy with lithium oxide left over. Repeatedly adding and removing hydrogen produced a nanocomposite with grain sizes of 20-30 nm. The researchers say that other elements that form stable metal hydrides could be used to make nanocomposite materials with this method, with potential applications not just in batteries but also in catalysis.